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Notes on the Measurement of pH Values

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The original definition of pH is:

$$\text{pH} = -\log a_{\text{H}}$$

Where a_{H} is the (relative) hydrogen ion activity. However, a single ion activity cannot be measured. Activities of individual ionic species are necessarily conventional. The pH number, of course, has in itself little absolute significance. As the negative of the logarithm of a product of a concentration (c or m) and an activity coefficient (γ or γ), it acquires its magnitude from the numerical scale adopted for the latter. Experimental pH measurements are nonetheless widely applied to the determination of thermodynamic equilibrium data such as pK values, on the assumption that they represent $-\log a_{\text{H}}$ (or $\text{p}a_{\text{H}}$). The single ion activity coefficient approaches unity as the ionic strength goes to zero, so that activity becomes m or c and $\text{p}a_{\text{H}}$ becomes $\text{p}m_{\text{H}}$ or $\text{p}c_{\text{H}}$.

pH is therefore defined *operationally* in terms of the operation or method used to measure it, that is, by means of a cell called an operational cell. The cell is standardized by solutions of assigned pH value (Reference Value pH Standard, Primary pH Standards and Operational Standards). Such standard reference solutions are buffer solutions whose pH values are assigned from measurements on cells with or without liquid junction. It must be emphasized that the definition of pH scale is quite different from the measurement of pH with glass-reference electrode-pH meter assemblies, where several standards are used in order to take into account possible deficiencies in the electrode and meter performance.

It is universally agreed that the definition of pH difference between two cells with different electrolytes is an operational difference, that is, the difference in electromotive force of the cells

Reference electrode | KCl (aq, concentrated) || solution X | H_2 | Pt

Reference electrode | KCl (aq, concentrated) || solution S | H_2 | Pt

Both cells (X and S) being at the same temperature and the hydrogen gas pressures and the reference electrodes being identical in the two cells. The two bridge solutions may be of any molality of potassium chloride not less than 3.5 mol kg/L, provided they are the same in both cells. There are three sources of potential difference in each cell. These are the potentials across the metal/solution phase boundaries at the hydrogen indicator electrode and the reference electrode and the liquid-junction potential across the liquid-liquid boundary. The liquid-junction potential arises from unequal diffusion of different ions in the two directions across the boundary.

The pH of solution X, denoted by pH(X), is then related to the pH of the standard reference solution S, denoted by pH(S), by the definition:

$$\text{pH(X)} = \text{pH(S)} + \frac{E(\text{S}) - E(\text{X})}{(RT/F) \ln 10}$$

Where R denotes the gas constant, T the thermodynamic temperature, F the Faraday constant, and E(S) and E(X) are the potentials of the cells of the standard and the test solutions respectively.

The definition above has quantitative significance as long as the liquid junction potential remains the same when solution S is replaced by solution X. For practical purposes, the hydrogen electrodes in both cells may be replaced by other hydrogen-ion-responsive electrodes, e.g. quinhydrone; in particular, in most measurements a single glass electrode, transferred between the cells, replaces the two hydrogen electrodes.

Considering the definition of pH given above, then the pH(X) of a solution using the cells described may be slightly dependent on which standard solution is used. In fact such variations in the measured pH(X) are usually at the 0.02 level and are too small to be of practical significance for most measurements.

When the objective is clearly the acquisition of thermodynamic data, the use of operational pH measurements is questionable. It can be said that as long as ionic strength does not exceed 0.1, pH measurements can be used to calculate thermodynamic data (such as pKa), but it has been shown to be remarkably useful for predicting thermodynamic properties of electrolytes in seawater at ionic strengths as high as 0.7.

Many, if not most, routine pH measurements do not fall in the category of dilute aqueous solutions. Important in commerce and industry are pH measurements in soils, brines, alcohol-water mixtures, suspensions, gels, tissues, and the like. In these cases, fundamental interpretations of the measured values in terms of hydrogen ion concentration are impossible and often unnecessary. The pH meter is standardized with aqueous reference solutions (buffer solutions), and therefore reproducibility is the prime consideration, and the numbers obtained by the meter are correctly understood as “the pH” of these diverse media.

Two different solutions (i. e. of different ionic strength or different ionic species) with the same pH value may have different hydrogen concentrations (so much different as allowed by the difference in their mean activity coefficients as their main source of dissimilarity). However these two solutions share the same operational pH value or the same hydrogen activity values (if we neglect the differences between the liquid junction potentials of the two solutions).

In short, values of pH obtained via pH-meters and glass electrodes of concentrated electrolytes are operational pH values and actually represent differences and similarities between the activity of hydrogen ions in these solutions. Thus, pH values of different electrolytes can be compared with each other as indication of their acidity or activity of proton levels.

For additional information or to emphasize the confidence of the reported pH values, workers measuring pH values should provide the following information about the measurements: a) Manufacturer and type of glass electrode and reference electrode. Method of forming the liquid junction of the reference electrode, b) Manufacturer and type of pH meter, and c) Method adopted to calibrate the pH meter system (i.e. type of standard/s and temperature).

Bibliography

1. The Modern Meaning of pH, Roger G. Bates, CRC Critical Reviews in Analytical Chemistry, pp. 247-178, January 1981
2. Definition of pH Scales, Standard Reference Values, Measurement of pH and Related Terminology, A.K. Covington, R. G. Bates and R. A. Durst, Pure & Applied Chemistry, Vol. 57, No. 3, pp. 531-542, 1985